Pressure-induced phase transformations in amorphous arsenic

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A B S T R A C T

The atomic structure of amorphous arsenic and its response to high pressure are explored using a constant pressure ab initio molecular dynamics technique. Different analyzing techniques reveal that amorphous arsenic has a local structure close to that of the crystalline phase. The model also presents some twofold and fourfold coordination defects. The existence of a possible amorphous to amorphous phase transition for arsenic is proposed on the bases of the observation of a gradual coordination increase with the application of pressure. Further compression of the amorphous state yields a transformation into a simple cubic crystal.

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1. Introduction

Arsenic (As) is one of the group-V elements with some interests. Its ground state is the rhombohedral A7 structure with covalent bonding. The A7 crystal has three nearest (intralayer) and three next (interlayer) neighbors and can be considered as a layer like structure. The A7 phase can be originated from a Peierls distorted simple cubic (SC) structure by a rhombohedral shear distortion along the [111] direction and an internal displacement of (111) planes toward each other in pairs along the [111] (Ref. [1]). The lowering symmetry from the SC phase to the rhombohedral A7 structure strongly reduces the electronic states near the Fermi level and a metal-to-semimetal transition is observed.

Amorphous form of arsenic (*a*-As) exists as well. It was investigated extensively in the past and valuable information regarding its atomic structure and physical properties was revealed in these studies [2–25]. Yet its response to high-pressure has been prompted in limited experiments so far. One experiment [21] stated a structural phase transition from an amorphous phase to an A7 structure at 4.0 kbar while the other [22] focused on simply the influence of pressure to the optical properties of *a*-As. Consequently, the high pressure behavior of *a*-As remains an open problem in solid state physics and materials science.

Both experimental and theoretical analyses [26–34] have shown an interesting phenomenon in some amorphous materials subjected to high pressure, viz. they undergo an amorphous-to-amorphous phase transformation, which is referred as polymorphism [26] and indicates the distinct amorphous states having different density and bonding

environments. Does such a phase transition occur in *a*-As as well? The main purpose of the present work is to find an answer to this question using a constant pressure molecular dynamics (MD) technique. Based on the results obtained through the MD simulations, the presence of amorphous-to-amorphous and amorphous-to-crystalline phase transformations is suggested for *a*-As.

2. Computational technique

The MD simulations were achieved by means of SIESTA ab initio code [35] based on the density functional theory (DFT) and a localized linear combination of atomic orbitals as basis sets. We used the Troullier and Martins approach to construct norm-conserving pseudopotential [36]. The exchange correlation energy was calculated by the generalized gradient approximation of PBE [37]. We adopted the double-ξ plus polarized basis set and Γ point sampling for the Brillouin zone integration for the calculations. The MD simulations were carried out using the NPT (constant number of atoms, constant pressure, and constant temperature) ensemble. One femtosecond (fs) was used for each MD time step. A randomly distributed disordered network having 160 atoms was chosen as a starting structure with the periodic boundary conditions. The initial random structure was subjected to a high temperature of 1150 K for 45.0 ps and its volume was adjusted by the Parrinello–Rahman method [38] but shear deformations were not allowed. The liquid state was cooled to 300 K in a period of 65.0 ps. The external pressure was increased gradually by an increment of 2.5 GPa. At each applied pressure, the amorphous model at 300 K was equilibrated for at least 15.0 ps. Temperature was controlled using the velocity rescaling

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method [39]. In order to visualize the structure, the VESTA program [40] was applied.

3. Results

The pair distribution function (PDF) provided in Fig. 1 allows us at some level to have an atomistic level description of a-As and to understand the impact of pressure on its local structural arrangements. At zero pressure, the first, second and third neighbor separations are located at 2.56 Å, 3.97 Å and 5.74 Å, respectively which are fairly close to the experimental results of 2.49 Å (X-ray) [23], 2.51 Å (neutron) [24], 3.78 Å (X-ray and neuron) [23,24] and 5.76 Å (X-ray) [23]. The minima in the PDF at 2.88 Å and 4.55 Å are also comparable with 2.9 Å and 4.6 Å reported in the X-ray study [23]. It should be noted here that the first peak position further accords with the first neighbor separations of 2.52 Å and 2.54 Å reported for the rhombohedral A7 crystal and liquid As [41], respectively. All these findings offer that our model fairly represents the atomic structure of a-As.

When the model is subjected to high pressure, the first peak position, as illustrated in Fig. 2, exhibits a quite complex behavior: generally it has a tendency to decrease under pressure but at some pressures it rapidly increases to a higher value. A close evaluation of the structure demonstrates that the abrupt change in the position is a result of the noticeable coordination increase at these pressures (see below). The behavior of the first peak position of a-As under pressure appears to be quite different from that of the compressed liquid and crystalline As [41]. Namely in the liquid state, the position of the first peak increases gradually and reaches almost a constant value above 10 GPa while in the crystal it uniformly decreases until the A7-to-SC phase change occurs at 35 GPa [41]. Consequently, a-As acts like a mixture of these two states when the trend of the first neighbor separation under pressure is considered. The PDF investigation and the visualization of the model (see Fig. 3) reveal that the system remains amorphous with some crystalline portions (SC type structure) at 25 GPa and it fully transforms to a crystalline phase as indicated by the appearance of pronounced peaks at long-range correlations at 27.5 GPa. As seen from Fig. 3, the crystal at 27.5 GPa has a SC structure having some distortions and structural defects.

The atomic structure of a-As and its response to the external pressure are additionally evaluated by the bond angle distribution function that is given in Fig. 4. At zero pressure, the distribution has a main peak around 97°, offering supportive evidence that a-As has a local environment similar to that of the A7 crystal. The large angles presented in the model are due to the twofold coordinated chain-like structures. With increasing pressure, the main peak gradually shifts toward to 90° and more large angles appear in the distribution, suggesting that the
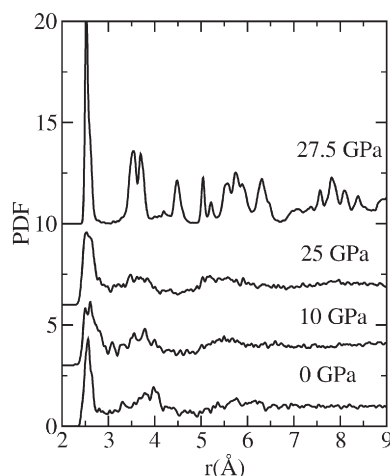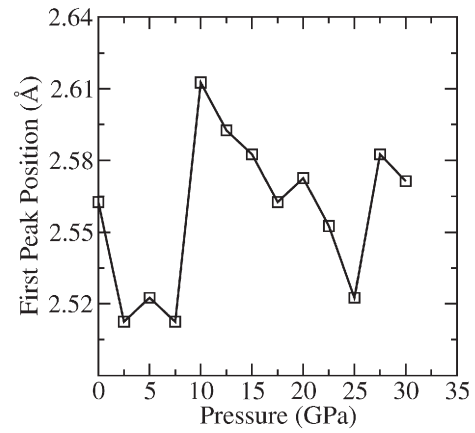

Fig. 2. Variation of the first neighbor separation as a function of pressure.

system has a tendency to form the octahedral-like configurations. At 27.5 GPa, the distribution has two main peaks around 90° and 180° as presented in a SC structure. The splitting of the peak near 90° is due to the distortion of the SC crystal.

The coordination number (CN) is a principal physical parameter and the pressure-induced phase transitions of materials are frequently identified by it. The average CN change and the coordination distributions as a function of pressure are shown in Fig. 5. At zero-pressure, 81% of atoms are found to be threefold coordinated. The fraction of the twofold and fourfold coordinated atoms is roughly 10% and 9% respectively. These fractions lead to an average CN of 2.97 at zero-pressure, which is reasonably close to that of the A7 crystal. As understood from Fig. 5, the CN of a-As is very sensitive to pressure and increases progressively with increasing pressure. Yet in some pressure regions (between 7.5 and 12.5 GPa) or at a pressure (27.5 GPa), the change is quite drastic. At 10 GPa the fourfold coordination becomes dominated. Further increase in pressure results into more fivefold and sixfold coordinated clusters As expected the system has mostly the sixfold configurations at 27.5 GPa.

In order to better understand the structural rearrangements in the short-range order under pressure and to find connections between the high-pressure amorphous state and the crystalline forms of As, it is essential to describe the geometry of the high coordinated clusters
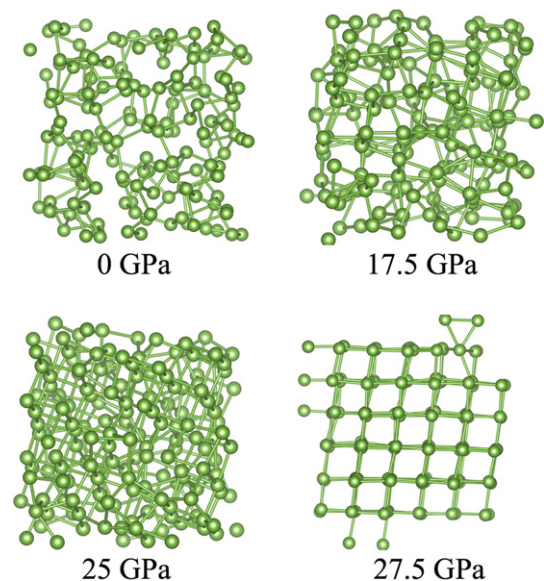

Fig. 1. Pair distribution function (PDF) at different pressures.

Fig. 3. Ball stick representation of arsenic obtained through the MD simulations at different pressures.